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PHYTOTOXICOLOGY SURVEY REPORT:
ASSESSMENT OF CHLORINE
IN TREE FOLIAGE
IN THE VICINITY OF DOMTAR
CORNWALL (1995)

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Ontario

Ministry of
Environment
and Energy

ISBN 0-7778-5753-7

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PHYTOTOXICOLOGY SURVEY REPORT:

ASSESSMENT OF CHLORINE IN TREE FOLIAGE

IN THE VICINITY OF DOMTAR

CORNWALL (1995)

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Executive Summary

In 1995, chlorine concentrations in maple foliage were elevated at sample sites close to Domtar, as well as at two sites about 2 km northeast of Domtar. These distant sites, particularly Site 22, had higher chlorine levels than sites in the immediate area of Domtar. And attempt will be made in 1996 to identify the source of chlorine in the east end of Cornwall. The overall mean chlorine concentration of the 16 maple sites used in the contour mapping decreased marginally from 1994 to 1995, but was markedly lower than 1986 and 1987. The chlorine level at 11 of the 16 sites was lower or unchanged from 1994. The extent of chlorine contamination in maple foliage to the east and northeast of Domtar also was reduced overall in 1995 compared to 1994. Foliar chlorine concentrations consistently higher than background occurred about 1300 m east, about 1500 m west and at least 1200 m north of Domtar.

Vegetation injury characteristic of chlorine was observed immediately northeast and east of Domtar. However, the severity of injury to sensitive vegetation in the survey area was less in 1995 relative to 1994. The foliar injury pattern in both years was consistent with chlorine emissions from Domtar being the main causal agent. ICI, the only other source of chlorine emissions in the general Domtar area, closed in March 1995. This likely contributed to the reduced chlorine levels at sites close to ICI's east fence in 1995.

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Phytotoxicology Survey Report: Assessment of Chlorine in Tree Foliage in the Vicinity of Domtar - Cornwall (1995)

Introduction

Vegetation in the vicinity of Domtar and ICI has been regularly analyzed for chlorine and inspected for foliar injury since 1985. Previous Phytotoxicology surveys indicated that Domtar was a chronic emitter of chlorine, while ICI was a more-localized, periodic, acute, chlorine source, as well as a mercury source. In March 1995, the ICI chlor-alkali plant (and mercury cell room) was closed, eliminating ICI as a potential source of chlorine. The status of ICI mercury emissions following the March closure is discussed in a separate report [Ref. 1]. The surveys were requested by the MOEE Eastern Region, Cornwall District office. This report presents the results of the 1995 chlorine survey. The results of earlier surveys have been separately reported.

Sampling / Inspections

On August 23 and 24 1995, foliage was sampled from 22 maple trees situated throughout the City of Cornwall at various distances downwind (east) and upwind (west) of Domtar (see Figure 1). Control sites in Ingleside, approximately 20 km west of Domtar, also were sampled. All foliage collection sites were the same as those used in 1994, with the exception of Site 4. Because of crowding by an adjacent tree, the Manitoba maple tree at Site 4 was replaced by the Manitoba maple in the backyard of the adjacent residential property to the south. At all sites, duplicate foliage samples were collected from middle branches exposed to Domtar, using standard MOEE procedures [Ref. 2). During the August survey, vegetation in the vicinity of each foliage collection site was inspected for chlorine injury. Vegetation at residences in the immediate vicinity of Domtar, and at more distant sites, also was inspected on July 18 1995.

All samples were returned to the Phytotoxicology processing laboratory. Here, the samples were dried and ground and then stored in glass jars. The samples were then submitted to the MOEE's Laboratory Services Branch at Resources Rd. for chlorine analysis.

Analytical Results

The chlorine analysis results (%, dry weight) for the period 1986 to 1995 are summarized in the attached table. The sample site numbers are unchanged from previous surveys so that direct comparisons can be made between years/reports. Over time, some survey sites were discontinued. Therefore, the site numbers in the table are not consecutive.

The 1995 tree foliage results, as in other years, revealed a pattern of elevated chlorine concentrations in the area of Domtar. This pattern is illustrated in Figure 2. In the area of Domtar, the highest chlorine levels were detected at Site 4 (0.68%) to the northeast, at Site 21 (0.63%) to the southeast, and at Site 14 (0.61%) to the northwest of Domtar.

As in previous years, foliar chlorine concentrations were even higher at Sites 22 (1.25%) and 32 (0.78%), about 2 km east of Domtar. These were the highest chlorine levels in the study, with the level at Site 22 being almost double the highest chlorine level at sites close to Domtar (1.25% versus 0.68%). This suggests that a chlorine source exists in the area of Site 22. This site is just east of the intersection of Second St. and Amelia St., while Site 32 is just north of the intersection of Fourth St. and Adolphus.

The five highest chlorine concentrations in each year from 1986 to 1995 are shaded in the results table. In six out of the nine years, the highest mean chlorine level occurred at Site 22. In 1995, the foliar chlorine concentration at Site 22 (1.25%) was the highest recorded since 1986.

Most sampling sites are close to a major road, and the possibility of the winter road salt applications having contributed to the foliar chlorine levels throughout the survey area can not be ruled out. However, if road salt is contributing to the foliar chlorine concentrations, the contribution must be marginal because there is still a clear chlorine gradient relative to Domtar. On the basis of the elevated chlorine levels at Sites 22 and 32, further investigation should be conducted to determine the local source. Domtar is not suspected to be involved because of the distance factor and because these sites are inconsistent with the chlorine concentration gradient around the pulp mill. These sites were old silver maple trees, and their old age combined with annual exposure to road salt may be involved in the elevated foliar chlorine levels. An attempt will be made in 1996 to identify the chlorine source in this area. In the interim, these two sites will be removed from the Domtar survey.

As a ULN (Upper Limit of Normal) guideline for chlorine in urban tree foliage has not been established, maple foliage collected from an upwind control location (Ingleside) was used as a basis for comparison. Foliage was collected from Manitoba, silver and Norway maples, as these were the most common species sampled in the Domtar survey. At the control site, the Norway maple sampled in 1986 had the highest chlorine level (0.34 %) over the nine years, and this level was used in the 1994 report as a guide in discussing the chlorine levels in the Domtar survey area [Ref. 3]. However, this would appear to be too high a control level to apply to silver or Manitoba maple trees. Nine years of replicated control data has shown that silver maple consistently has the lowest foliar chlorine concentrations, that the chlorine content of Manitoba maple leaves is consistently almost twice that of silver maple, and that Norway maple, on average, has foliar chlorine concentrations that are consistently about twice as high as Manitoba maple. When tested statistically it was found that the nine-year mean foliar chlorine concentrations from the Ingleside control site for the three maple species were significantly different from each other ($p<0.001$). Since Norway maple foliage has high natural chlorine concentrations it may not be a reliable monitor of relatively low ambient air chlorine levels, and therefore the Norway maple data has been removed from the 1995 Domtar survey results.

Eleven of the 16 remaining sampling sites had chlorine levels that were lower or unchanged in 1995 relative to 1994. In 1995, Sites 1, 6, 9, and 16 had the lowest levels since the survey started, while Sites 22, 23 and 32 had the highest chlorine levels detected at these sites. The ICI chlor-alkali plant closure likely contributed to the lower chlorine level at Site 1 in 1995, as this site was situated adjacent to ICI's east fence.

Figures 2 and 3 compare the respective 1995 and 1994 chlorine contamination contours relative to Domtar. These contours maps do not include Sites 22 and 32 (area of anomalously high chlorine 2 km east of Domtar) and Norway maple Sites 14, 19, 33 and 37. The Norway maples were excluded as the Ingleside control site indicated that Norway maple foliage may not be a reliable monitor of low ambient air chlorine levels. The contour maps were derived using the Surfer computer software program. The chlorine contamination contours in these figures are estimates, the actual concentrations are known only at the sample sites. The lowest contour value, 0.2%, is about double the highest foliar chlorine concentration encountered in silver or Manitoba maple at the Ingleside control site. Therefore, foliar chlorine levels above 0.2% for these two maple species are unquestionably higher than background and likely reflect exposure to an industrial source of chlorine.

Figures 2 and 3 show that the extent of chlorine contamination in tree foliage to the east and northeast of Domtar was reduced overall in 1995 relative to 1994. This is not surprising as 11 of the 16 sites used to generate the contour maps had chlorine levels that were lower or unchanged in 1995.

In 1995, foliar chlorine concentrations consistently higher than background occurred about 1300 m east, about 1500 m west and at least 1200 m north of Domtar. The 1995 map (Figure 2) clearly illustrates a chlorine concentration gradient relative to Domtar. In contrast, in 1994 (Figure 3), although the highest chlorine levels occurred near Domtar, elevated foliar chlorine concentrations were clearly evident in the residential community immediately east of ICI. This contamination largely disappears in 1995, which is coincident with the closure of ICI's mercury cell chlor-alkali plant.

These data reaffirm the conclusions of earlier Phytotoxicology reports, i.e., that Domtar is the main chlorine source and ICI is a secondary, more localized chlorine source.

Chlorine emissions from Domtar (mainly) originate from a stack, which tends to distribute the contaminant over a larger area, whereas chlorine from ICI was (mainly) emitted through roof vents from the cell room, which was closer to ground level and tended to dissipate into the local adjacent residential community. The absolute extent of chlorine contamination in Cornwall didn't change much between 1995 and 1994 (because chlorine is still being emitted from the Domtar stack), but the chlorine gradient is much steeper in 1995, particularly in the residential community around Gulf and Yates Ave. between Third and Fifth Sts., which reflects the closure of the ICI cell rooms.

Observations in July and August

The inspections over the broader survey area in July and August (1995) revealed the most severe chlorine-type injury on vegetation in the residential area immediately east to northeast of Domtar. This pattern, together with the ICI chlor-alkali plant closure prior to the growing season, implicated Domtar emissions as the cause. As in 1993 and 1994, the most severe chlorine-type injury was observed on hydrangea foliage in the area of Third St. and Gulf Ave. (north of Second St.) and on tomato foliage in the area of Brookdale Ave. and Smith St.(south of Second St.). Hydrangea foliage is particularly sensitive and was used to determine the extent of the injury in 1995. In 1995, hydrangea was injured to the northeast of Domtar through to the area of Munro St. and Third St. (between Brookdale and Cumberland).

The injured hydrangea plants had blackish stipples scattered over the upper surface of three to four older leaves. With most leaves being healthy, the overall injury to the most adversely affected hydrangea plants was of trace to very light severity overall. Stippling on upper-leaf-surfaces is typical of oxidant injury (chlorine is an oxidant, as is ozone)[Ref. 4]. The hydrangea foliage in the area of Third St. and Gulf Ave. had severe stippling in 1993 and 1994, with most hydrangea leaves, including younger leaves, being affected. The tomato plants most adversely injured had undersurface chlorine-type injury on several older middle leaves, and light to moderate plant injury overall. Rhubarb is chlorine-sensitive in early stages of growth but, unlike in 1994, chlorine injury on rhubarb foliage was not observed in the Domtar survey area in 1995. Overall, the severity of vegetation injury in the survey area was less in 1995 relative to 1994.

The 1995 ozone data from the MOEE ozone monitoring station in Cornwall was examined, as chlorine injury on vegetation is similar to ozone injury, and as tomato plants in particular are known to be sensitive to ozone. The ozone monitoring station is located in the vicinity of Third St. and Cumberland Ave., to the northeast of Domtar. Air monitoring for chlorine is not routinely performed in Cornwall. The MOEE operates a network of ozone monitors across the province, as ambient ozone levels are regularly elevated, especially during the summer months. In Cornwall, from June 1 through August 24 (1995), the MOEE's 80 ppb (parts per billion) one-hour ozone criterion, which was developed to protect sensitive vegetation, was exceeded in the afternoon of June 7 for 5 hours, June 17 for 4 hours, June 18 for 7 hours, July 13 for 9 hours, and on August 1 for 1 hour. Hence, during the 1995 growing season, there were several periods when ambient ozone levels in Cornwall were potentially injurious to sensitive vegetation. However, as the hydrangea injury in July and August was confined to residences in the immediate area and downwind of Domtar, chlorine emissions from Domtar are suspected to be the main causal agent. If ozone was responsible, then the hydrangea injury would be widespread across the city, rather than localized in the area of Domtar, as ozone is a regional air pollutant and is not associated with a specific industrial source. The injury severity on the tomato plants just east of Domtar in July also was likely due to chlorine. In mid-July (1995), tomato crops were surveyed for ozone injury in central and southwestern Ontario, where ozone levels are generally higher during the summer. At all survey locations in Central and Southwestern Ontario, the ozone injury severity on affected tomato plants was trace to very light overall. The more severe tomato injury (light to moderate) in July to the east of Domtar is in contrast to the general trend elsewhere in the province and substantiates the conclusion that chlorine was the causal agent of plant injury in Cornwall. The 1994 results also implicated chlorine as opposed to ozone, because in 1994 the hydrangea injury at Gulf Ave. and Third St. was considerably more severe than 1995 but the MOEE's one-hour ozone criterion (80 ppb) was exceeded only for four hours during the 1994 growing season (May 1 through August 24). Three of the exceedences occurred in August over a month after the hydrangea injury was initially observed (June 28 1994). The earlier exceedence on May 30 (82 ppb) would not have caused the severe injury that was present on hydrangea foliage in late June of 1994.

The phytotoxicology surveys (1986 to 1995) confirm that Domtar emits chlorine into the atmosphere. Kraft mills, like Domtar, also can emit precursor chemicals (eg. monoterpenes) that can undergo photochemical reactions in the atmosphere and produce ozone and PAN (peroxyacetyl nitrate)[Ref. 5]. PAN injury on vegetation is similar to chlorine [Ref. 2]. However, PAN is not suspected to be involved because of the close proximity of the affected properties to Domtar. Ozone and PAN related to pulp mill emissions takes time to form in the atmosphere and elevated ambient air concentrations occur at distances downwind of the source of precursors. Also, PAN injury on vegetation has never been documented in Ontario. Therefore, it is concluded that chlorine emissions from Domtar were responsible for the oxidant injury that was observed on sensitive vegetation in 1995.

Conclusion

In 1995, chlorine concentrations in maple foliage were elevated at sample sites close to Domtar, as well as at two sites about 2 km northeast of Domtar. These distant sites, particularly Site 22, had higher chlorine levels than sites in the immediate area of Domtar. An attempt will be made in 1996 to identify the source of chlorine in the east end of Cornwall. The overall mean chlorine concentration of the 16 sites used in the contour mapping decreased marginally from 1994 to 1995, but was markedly lower than 1986 and 1987. In 1995, the chlorine level at 11 of the 16 sites was lower or unchanged from 1994. The extent of foliar chlorine contamination to the east and northeast of Domtar also was reduced overall in 1995. Foliar chlorine concentrations consistently higher than background occurred about 1300 m east, about 1500 m west and at least 1200 m north of Domtar.

As in previous years, vegetation injury characteristic of chlorine was observed immediately northeast and east of Domtar. However, the severity of injury to sensitive vegetation in Cornwall was less in 1995 relative to 1994. The foliar injury pattern in 1995 was consistent with Domtar emissions being the main causal agent. ICI, the only other source of chlorine emissions in the general Domtar area, closed in March 1995. This likely contributed to the reduced chlorine levels at sites close to ICI's east fence.

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Chlorine Concentrations* in Tree Foliage: Cornwall (1986-1995)

Site	Distance***	Maple	1986	1987	1989	1990	1991	1992	1993	1994	1995
1**	670 N	Silver	0.33	0.39	0.20	0.18	0.21	0.23	0.37	0.24	0.14
2**	670 NNE	Manitoba	0.34	0.38	0.25	0.24	0.20	0.30	0.22	0.40	0.26
4**	420 NE	Manitoba	0.96	1.15	0.50	0.59	0.39	0.24	0.44	0.53	0.68
6**	600 NE	Sugar	0.34	0.29	0.18	0.19	0.21	0.21	0.15	0.19	0.10
8**	690 NE	Red	0.26	0.25	0.13	0.15	0.22	0.25	0.20	0.29	0.14
9**	810 NE	Silver	0.68	0.57	0.40	0.37	0.53	0.43	0.46	0.41	0.36
10**	1060 NE	Silver	0.28	0.26	0.25	0.20	0.29	0.39	0.28	0.27	0.27
11**	1370 NE	Silver	0.42	0.34	0.09	0.15	0.16	0.18	0.14	0.26	0.12
12**	960 NNW	Silver	0.21	0.75	0.20	0.15	0.30	0.32	0.26	0.25	0.36
16**	710 E	Silver	0.18	0.17	0.09	0.10	0.11	0.07	0.10	0.05	0.04
21**	540 SE	Silver	0.80	0.78	0.27	0.27	0.34	0.43	0.35	0.59	0.63
23**	1100 N	Silver	0.23	0.21	0.10	0.13	0.13	0.24	0.22	0.25	0.29
25**	1730 NNE	Manitoba	0.21	0.23	0.26	0.19	0.23	0.13	0.26	0.36	0.29
27**	920 E	Silver	0.45	0.44	0.24	0.29	0.32	0.34	0.52	0.40	0.37
35**	1620 WSW	Silver	0.32	0.28	0.16	0.10	0.20	0.24	0.16	0.18	0.15
36**	2580 NE	Manitoba	0.20	0.17	0.09	0.12	0.16	0.14	0.12	0.16	0.17
Mean			**0.39**	**0.42**	**0.21**	**0.21**	**0.25**	**0.26**	**0.27**	**0.30**	**0.27**
Sites Excluded from Contour Maps											
22	1810 ENE	Silver	0.60	0.57	1.00	1.20	0.83	1.05	1.10	0.77	1.25
32**	2000 NE	Silver	0.54	0.64	0.62	0.45	0.53	0.33	0.61	0.78	0.78
14**	210 NW	Norway	0.94	0.75	0.77	0.68	0.71	0.75	0.47	0.42	0.61
19	580 WSW	Norway	0.34	0.27	0.15	0.24	0.30	0.22	0.29	0.36	0.34
33**	790 NW	Norway	0.64	0.68	0.36	0.28	0.50	0.20	0.39	0.37	0.54
37**	3700 NE	Norway	0.36	0.32	0.43	0.29	0.56	0.27	0.33	0.36	0.44
Controls (Ingleside)		Manitoba	0.11	0.12	0.10	0.06	0.05	0.09	0.08	0.05	0.11
		Silver	0.06	0.03	0.02	0.04	0.02	0.06	0.05	0.04	0.07
		Norway	0.34	NR	0.21	0.14	0.11	0.17	0.12	0.18	0.19

* Percent dry weight, mean of duplicate samples and analysis. *** Distance (meters) and direction from Domtar NR - No samples collected.

** Same foliage type was collected at original site or nearby site in all years **Note**: Shaded results were the five highest each year.

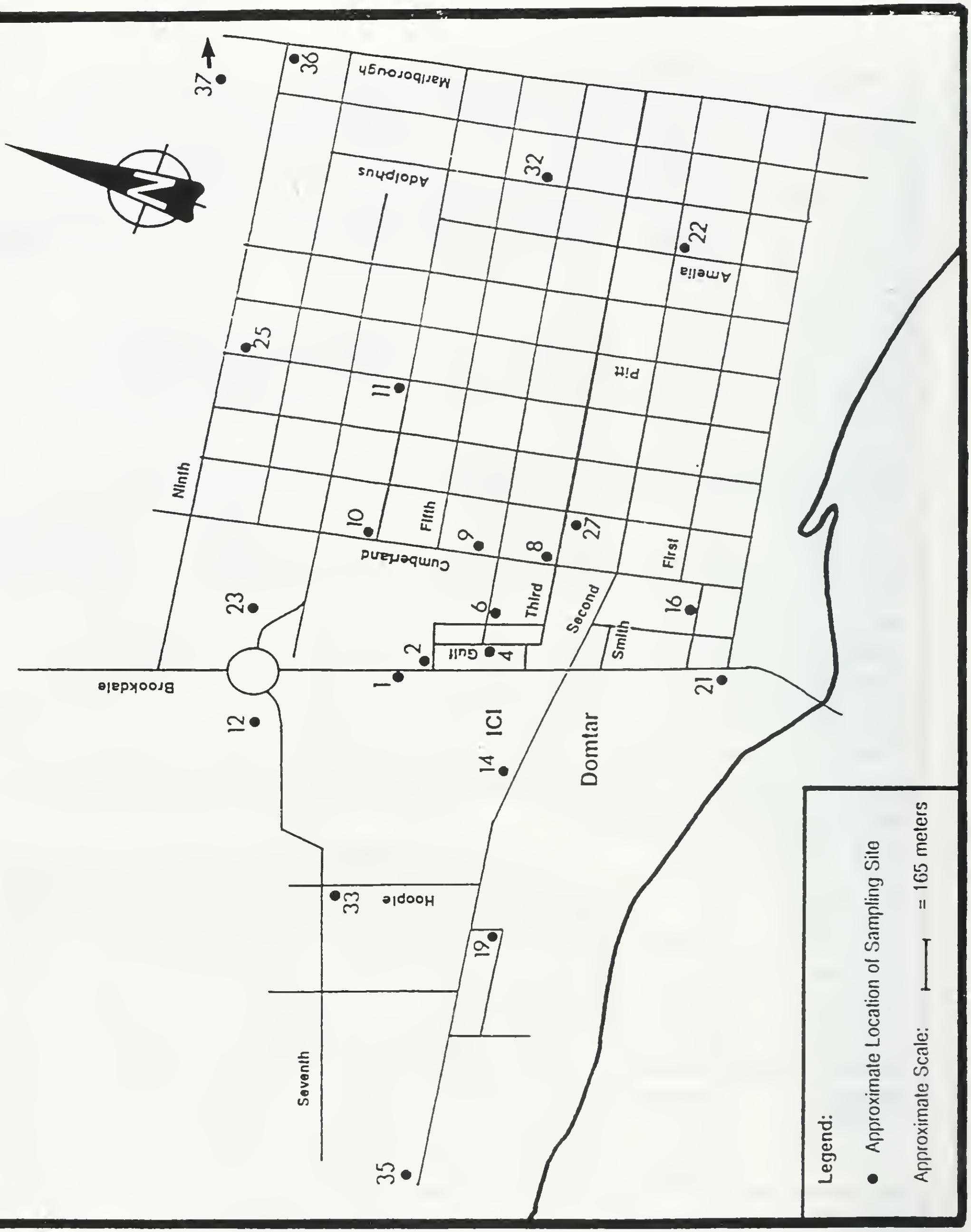
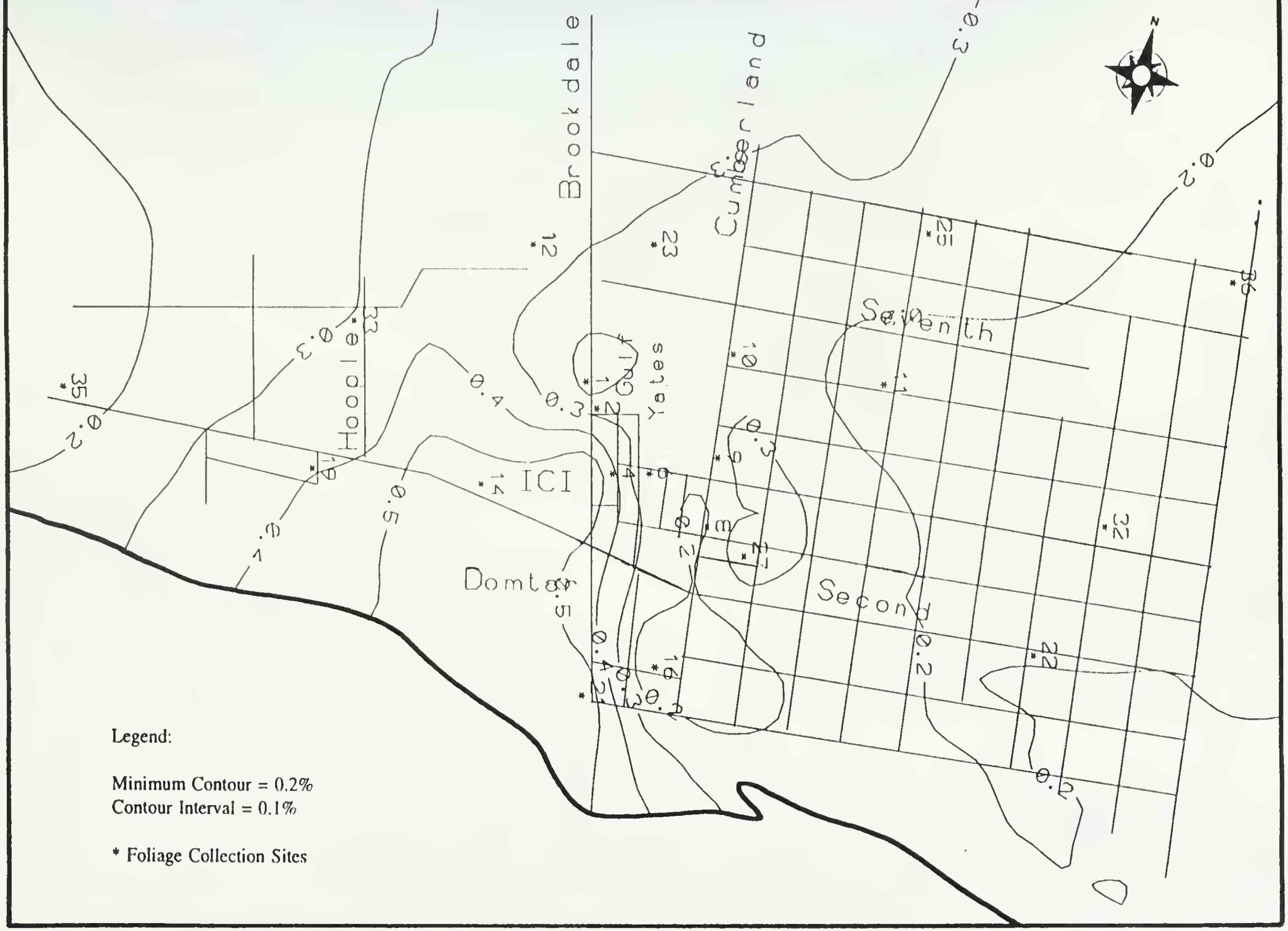


Figure 1: Tree Foliage Sites in Relation to Domtar, Cornwall (1995).

Figure 2: Chlorine in Maple Foliage: Cornwall (1995).



Legend:

Minimum Contour = 0.2%
Contour Interval = 0.1%

* Foliage Collection Sites

Figure 3: Chlorine in Maple Foliage: Cornwall (1994).